Positron annihilation studies of the iron-substituted oxide superconductor $YBa_2(Cu_{1-x}Fe_x)_3O_{7-y}$

LETTER TO THE EDITOR

Positron annihilation studies of the iron-substituted oxide superconductor YBa$_2$(Cu$_{1-x}$Fe$_x$)$_3$O$_{7-y}$

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Abstract. Positron lifetime measurements were performed on YBa$_2$(Cu$_{1-x}$Fe$_x$)$_3$O$_{7-y}$ with $x = 0, 0.01, 0.02, 0.03, 0.06, 0.09$ and 0.12 as a function of temperature between 20 K and room temperature. The positron mean lifetime and its thermal behaviour strongly depend on the iron concentration. A plausible model is proposed, in which the observed results are explained in terms of positron weak localisation due to copper–oxygen chain disordering.

Positron annihilation methods have been applied in studying various problems in condensed matter such as Fermi surfaces, lattice defects and phase transitions, and have shown their usefulness (West 1973, Hautojarvi 1979, Brandt and Dupasquier 1983). Superconducting metals and alloys have also been studied by positron annihilation methods (Stump and Talley 1954, Green and Madansky 1956, Shafroth and Marcus 1956), but no significant changes in positron annihilation parameters between the superconducting and normal states were found, against theoretical prediction (Dresden 1954, Tripathy and Bhuyan 1985). Dresden suggested that the change in electron distribution or the reduction of the triplet to singlet conversion and the pick-off annihilation of the positronium lengthen the positron lifetime with the superconducting transition. Tripathy and Bhuyan mentioned that the positron lifetime increases in the superconducting state due to superconducting gap formation which causes a change in positron–electron correlation and, as a result, a decrease in the electron density enhancement.

Several oxide superconductors—for example, La–Sr–Cu–O (Kishio *et al* 1987), Y–Ba–Cu–O (Wu *et al* 1987), Bi–Sr–Ca–Cu–O (Maeda *et al* 1988) and Tl–Ba–Ca–Cu–O (Sheng and Hermann 1988)—have been discovered since Bednorz and Müller (1986) reported the superconductivity of the La–Ba–Cu–O system. The positron annihilation parameters change in a quite different manner in some of these oxides. Our previous work (Ishibashi *et al* 1987, 1988) firstly reported anomalous behaviour of the Doppler broadening line shape parameter around the superconducting transition temperatures

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in La–Sr–Cu–O and Y–Ba–Cu–O. Jean *et al* (1987) reported an onset increase of positron lifetime as well as the Doppler broadening S-parameter near the transition temperature. Subsequently, a number of positron studies have been published, mainly on $YBa_2Cu_3O_7$, and have shown a large variation in the results, as reviewed by Manuel (1989), who mentioned that the granularity of the source powder, heat treatment, homogeneity and eventual second phase are important factors for the variation of positron annihilation parameters. Such factors are reflected in the microstructure and the amount and/or the type of lattice defects existing in the samples. Several kinds of defect may act as positron trapping centres according to the calculation by Jensen *et al* (1989). Then, the variation of defects leads to the variation of positron annihilation properties. In fact, Usmar *et al* (1988) reported a correlation between the microstructure of their samples and the positron lifetime or the temperature dependence of the Doppler broadening S-parameter. Corbel *et al* (1989) mentioned the effect of annealing stages in oxygen.

Systematic experiments are required on well characterised samples to study oxide superconductors by the positron annihilation techniques since the amounts and types of sites where a positron annihilates are significant problems. In this letter, we present the results of positron lifetime measurements on the iron-substituted oxide superconductor $YBa_2(Cu_{1-x}Fe_x)_3O_{7-y}$ ($0 \leqslant x \leqslant 0.12$) as a function of temperature between 20 K and room temperature. There are two reasons for choosing these materials. One is to clarify the relationship between the temperature variation of the positron mean lifetime and the superconducting transition temperature; substitution for copper with iron depresses the transition temperature as a function of iron concentration. The other is to examine the effects of microstructural change induced by iron doping—mainly, disordering of copper–oxygen one-dimensional chains.

Samples of $YBa_2(Cu_{1-x}Fe_x)_3O_{7-y}$ with $x = 0, 0.01, 0.02, 0.03, 0.06, 0.09$ and 0.12 were prepared by solid state reaction. The starting materials were high-purity powders of Y_2O_3, $BaCO_3$, CuO and Fe_2O_3. The powders were thoroughly mixed in the nominal compositions and calcined first at 910 °C for 10 h, secondly in the same conditions and finally at 920 °C for 10 h, with pulverisation between the calcination steps. The reacted samples were pulverised again, pressed into pellets with a diameter of $\simeq 8.8$ mm and thickness of $\simeq 1.5$ mm, then heated to 750 °C in vacuum and maintained there for 1 h. These evacuation steps are to remove the contamination of the powders with moisture and/or carbonic acid gas thoroughly. Then, the samples were heated again to 930 °C in an O_2 flow and sintered for 20 h; this was followed by annealing at 400 °C for 10 h. These samples were characterised by the x-ray diffraction method and resistivity measurements using a conventional DC four-probe method.

Figure 1 shows variations of the lattice parameters with x for $YBa_2(Cu_{1-x}Fe_x)_3O_{7-y}$. As already reported (Maeno *et al* 1987, Tarascon *et al* 1988), a structural change from orthorhombic to tetragonal occurs with increasing x. The results of resistivity measurements are shown in figure 2. The observed superconducting transition temperatures for each x were shifted up slightly in comparison with the values previously reported by Maeno and Fujita (1988) but agree with the results of Tarascon *et al* (1988).

The lifetime spectra were measured using a fast–fast lifetime spectrometer with a resolution of 190–220 ps full width at half maximum (FWHM). The positron source was prepared by depositing a $^{22}NaCl$ solution on a Kapton sheet with a thickness of 7.5 μm and covered with another Kapton sheet. To observe the temperature effects, the samples were cooled with a helium cryogenic apparatus in a vacuum chamber. The temperature was varied between 20 K and room temperature and monitored with a Au(0.07at.%Fe)/ chromel thermocouple. About 10^6 counts were accumulated for each spectrum.

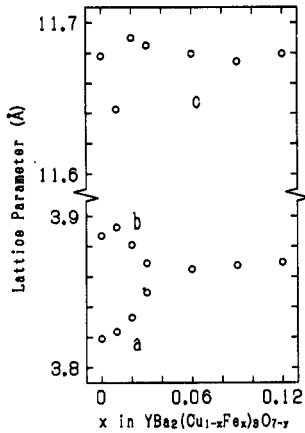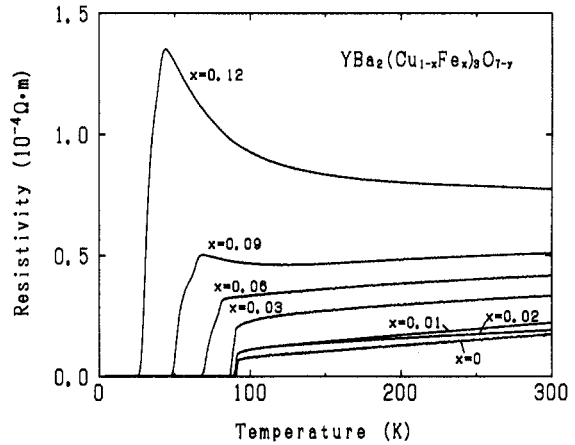**Figure 1.** Variations of the lattice parameters with x for $YBa_2(Cu_{1-x}Fe_x)_3O_{7-y}$.

Figure 2. Electrical resistivity as a function of temperature for $YBa_2(Cu_{1-x}Fe_x)_3O_{7-y}$ with $x = 0, 0.01, 0.02, 0.03, 0.06, 0.09$ and 0.12.

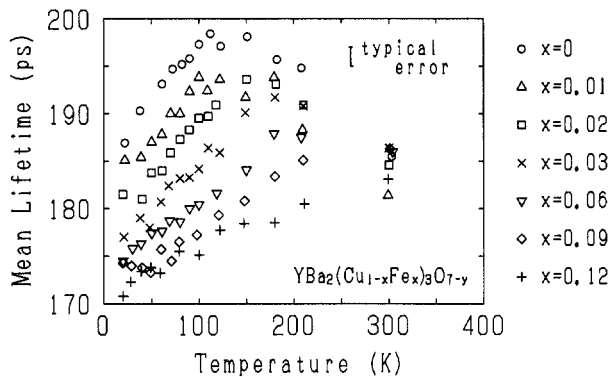**Figure 3.** Positron mean lifetime as a function of temperature for $YBa_2(Cu_{1-x}Fe_x)_3O_{7-y}$ with $x = 0, 0.01, 0.02, 0.03, 0.06, 0.09$ and 0.12.

The spectra obtained were analysed using the PATFIT program (Kirkegaard *et al* 1981) and divided into two components of 110–160 ps and 210–300 ps, together with a source component of 376 ps with an intensity of 20.2%. Each value of these two components was subject to large scatter with change of temperature because of insufficient statistics. We have calculated the mean lifetime, which is insensitive to the details of the separation of the individual components (Virtue *et al* 1978). The results are shown in figure 3 against the temperature. The thermal behaviour of the mean lifetime of the undoped sample is qualitatively in agreement with the previous results on the mean lifetime (Moser and Henry 1989) and the S-parameter (Lynn *et al* 1988, von Stetten *et al* 1988, Brusa *et al* 1988). That is, the mean lifetime increases with temperature in the temperature range to 110 K, is nearly constant between 110 K and 150 K, and then decreases to the value 185 ps. Iron doping induced a systematic change in the positron mean lifetime. The mean lifetime decreased with iron concentration increasing at all temperatures except

room temperature, at which all the lifetime values became close to each other and fell into the range 180–185 ps. Additionally, some other characteristic phenomena were observed. The saturation temperature of the mean lifetime as well as the temperature where the lifetime began to decrease shifted up systematically with increasing iron content. A decrease of the temperature coefficient of the lifetime was also observed.

Existence of a discontinuity in the mean lifetime at the superconducting transition temperature was not clear from the present experiments. No anomalous change exceeding the experimental error was observed. Increase in the lower-temperature region cannot be attributed to the superconducting state of the specimens because the increase itself continues beyond the superconducting transition temperature for higher-x samples.

One plausible origin for this increase is a weak localisation of positrons—in other words, a shallow trapping of positrons (Moser and Henry 1989). Shallow trapping coexisting with deeper trapping brings about an increase of mean positron lifetime with temperature, as previously reported for silver by Linderoth and Hidalgo (1987). A positron localised at a shallow centre escapes from it via thermal activation. Then, the contribution of positrons trapped at shallow centres to the total annihilation decreases with increasing temperature. Since the positron lifetime in the shallow trap is usually shorter than that in the deeper trap, the mean lifetime is expected to increase with temperature. The positron distribution in $YBa_2Cu_3O_7$ was calculated to be quasi-one-dimensional along copper–oxygen one-dimensional chains (von Stetten *et al* 1988, Bharathi *et al* 1989, Singh *et al* 1989, Jensen *et al* 1989). Therefore, it is expected that weak localisation of positrons is caused by the disorder of this one-dimensional path of positrons between the chains due to defects such as twin boundaries.

Iron doping causes a structural phase transition from orthorhombic to tetragonal (Maeno and Fujita 1988, Tarascon *et al* 1988). This phenomenon correlates with micro-structural changes from a parallel twin structure to a microdomain structure as a result of copper–oxygen chain disordering (Hiroi *et al* 1988). The length of the one-dimensional path of the positron decreases with increasing degree of the disorder, and therefore the shallow trapping of positrons is expected to be enhanced with x. Observed variations of the positron lifetime and its thermal behaviour with variation in x can be explained within this scheme. These lifetime variations with x are more distinct in the orthorhombic (low-x) region than in the tetragonal (high-x) one, as shown in figure 3. This may be related to the experimental fact that twin boundary spacing or domain size decreases monotonically in the orthorhombic region and is nearly constant in the tetragonal region (Wördenweber *et al* 1989).

The deeper trapping centre is still open to question. Oxygen vacancies were proposed to provide such a centre in early studies, but the resulting specific trapping rate was too low. Jensen *et al* (1989) calculated positron lifetimes for defects in $YBa_2Cu_3O_7$ as well as bulk lifetimes in $YBa_2Cu_3O_6$, $O_{6.5}$ and O_7. They suggested that metal vacancies are responsible for lifetimes of more than 200 ps. Moser and Henry (1989) claimed CuO divacancy. Balogh *et al* (1988) reported a significant change in positron annihilation parameters at $\simeq 240$ K. They attributed it to a structural change. Brusa *et al* (1988) tried to explain their result that the S-parameter showed a sudden decrease around 240 K with thermal detrapping of positrons. In the present work, reductions or saturations of the positron mean lifetime above 150 K were observed. If we assume this behaviour of the mean lifetime to be due to thermal detrapping, the observed shift of the temperature at which the lifetime begins to decrease can be attributed to an increase in positron binding energy to the deeper trap. There are many experimental results, however, that

indicate no change in lifetime in such a temperature region. More systematic work is needed.

In summary, we observed a strong dependence of the positron mean lifetime and its thermal behaviour on the iron concentration x for $YBa_2(Cu_{1-x}Fe_x)_3O_7$. The results are explained using a model in which disordering of copper–oxygen chains causes a weak localisation of positrons that leads to the decrease in the contribution of positron annihilation at the deeper trap to the mean lifetime. The shift of the temperature where the mean lifetime begins to decrease was tentatively assigned to an increase of positron binding energy to the deeper trap with increasing iron concentration. It is worthwhile to investigate positron parameters for specimens containing other dopants such as cobalt, aluminium, nickel and zinc for the purpose of examining the validity of the model. All the dopants, including iron, depress the superconducting transition temperature. There are some differences as regards the preferential site and the effect on microstructure among the dopants (Maeno and Fujita 1988, Tarascon *et al* 1988, Kajitani *et al* 1988). Iron occupies both the Cu(1) site on the one-dimensional chain and the Cu(2) site on the two-dimensional plane, and the contribution of the Cu(1) site decreases with decreasing oxygen atmosphere in the sintering process. Cobalt atoms occupy the Cu(1) site while nickel atoms occupy the Cu(2) sites. Zinc atoms substitute for copper atoms on both sites with occupancies of 0.20 and 0.05 when Cu:Zn = 2.7:0.3. Iron and cobalt atoms disorder the copper–oxygen chain and cause the orthorhombic–tetragonal structural transition while nickel and zinc atoms do not. Then, we can investigate the effects of the superconducting transition and the microstructural change on the positron parameters separately. Some experimentation is now in progress.

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